Chemical Structure and Processing of Coal

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During the past several years, much excellent work has been done which contributes to a more complete knowledge of the basic structure of coal. Smirnov (1) states in a comprehensive review article that there has been a development and deepening of our knowledge of coal structure, an increase in the number of investigations and a broadening of the circle of scientists from different countries occupied with these questions.

The Model for High Volatile Bituminous coal, suggested in Figure 1, takes into account the major observations reported in the literature as well as observations made in our laboratory (2).

The model suggests that coal consists of large heterocyclic nuclei (with alkyl side chains) monomers, held together by the three dimensional C-C groups suggested by Friedel (3), the functional oxygen groups of Van Krevelen (4), and the ether bonds of Kukharenko (1), Roy (5), Blom (6), Brooks (7) and Orchin and Storch (8, 9, 10, 11). Sulfur is interchangeable with oxygen in some structures and the close relationship between the chemical properties of similar fractions suggests that sulfur and oxygen may be present in linking units. All researchers seem to agree that nitrogen occurs mainly in the heterocyclic ring structures. (12).

The functional oxygen groups in coal are best presented by Blom, Edelhausen, and Van Krevelen in their functional oxygen group diagram (6). Van Krevelen's method of calculating the functional oxygen groups by the amount of water, carbon dioxide and carbon monoxide derived from primary carbonization was applied to the gases obtained from low temperature carbonization of a Utah semi-coking coal (13). The results are as follow: OH = 6.4 to 7.8%, COOH = 0.5 to 1.0%, -O- and C = O = 1.3 to 2.6%. These percentages agree with the proposed model.

The nature of the "hydrocarbon" components of the coal structure has been discussed by Nelson (14). His evaluation of the work of Frolich and Fulton on coals heated to temperatures of 750°F to 1100°F is the partial basis for concluding that long chain, simple, aliphatic and alicyclic hydrocarbons groups predominate in the coal structure. Other evidence is found in the work of Goodman, Gomez and Parry (15, 16) who find high yields of olefins and paraffins in their low temperature carbonization distillates. The amount of olefins found in low temperature

tars may be as high as 50% of the neutral oil yield. Olefins and paraffins combined in a typical sample of distillate from a high volatile bituminous B coal from Spring Canyon Utah totalled 64% (Ibid.)

The normal and isoparaffin content of low temperature tars is reported by Lewis. He identified C_9 to C_{22} normal paraffins and C_{10} to C_{17} isoparaffins in the products of low temperature distillation (17).

A sample of crystalline hydrocarbon from low temperature carbonization was furnished our laboratory by the Pacific Chemical Company of Wellington, Utah. The material had been assumed to be a pure aromatic fraction; infra-red analysis and other tests demonstrated it to be essentially a C_{20} paraffin. The total distillate from this operation was atypical of coal tars; it resembled a waxy gas-oil-creosote oil mixture and was reddish-brown in color. Apparently little secondary cracking and polymerization had occurred in the process of its formation.

Friedel and Queiser, by ultra-violet and visible spectra studies concluded that aliphatic groups rather than poly nuclear condensed aromatics predominate in the coal structure (3,12).Given (18) and Brown (19, 20) present evidence for polycondensed aromatics. It may be that coals can vary in the relative amounts of hydrocarbon class constituents as do different crude oils.

The structures tying together the components constituting coal are considered by Given (18), Van Krevelen (1, 21, 22, 23) and Dryden (24) to be principally aliphatic (methylene) bridges. Friedel and Queiser (3) believe that tetrahedral bonds are the cross linking units required to give coal its three dimensional structure. Brown et al., from nuclear magnetic resonance studies and from infra-red studies on coal distillates, found little evidence for methylene bridge carbons (19, 20). The structure proposed in the present paper conforms to these observations.

There seems to be a general belief that the larger the organic molecule the more complex it becomes. This belief is probably a logical consequence of the increase in the number of theoretically possible isomers with increase in molecular weight and the difficulty of separating the large molecules. However, Hood and associates from mass spectrometric studies of heavy distillates of petroleum (e.g. C_{20}-C_{40} oils and waxes) during the past several years present a different picture. They find the molecules contain essentially one long carbon-atom chain, to one or both ends of which a ring system or short branch may be attached. In paraffin waxes the molecules are predominantly n-alkanes along with some slightly branched iso-alkanes, cycloalkanes, and even traces of aromatics. In lubricating oils, the isoalkanes have slightly longer branches, and the monocycloalkanes and monoaromatics have several short methyl branches on the ring.

Polyaromatics generally appear to have all of their aromatic rings in a single condensed nucleus. Similarly, mass spectral evidence for polycyclic saturates suggests molecules with a condensed ring system at one end of a chain, but the interpretations are less clear and cannot yet exclude the possibility of a ring systems at both ends. Although it is recognized that a small percentage of complex molecules might be present, the authors consider the new picture to be one which, in general, is representative of the distillate range of petroleum ($< C_{40}$) (25). This concept of simplicity and lack of isomers of large molecules is probably true in the basic structure of coal as well. In coal the large condensed nuclei are hetrocyclics with the same simple aliphatic side chains.

Structure and Distillation

From the work of Orchin, Storch and associates (9, 10, 11, 26), Frankè, Crowley and Elder (27), Gomez, Goodman and Parry (15, 16), Berkowitz (28, 29) and Van Krevelen and associates (4), it can be seen that the yield of liquids from coal distillation is dependent upon the basic structure of the coal, particularly the functional groups, and the process used to convert the coal into liquids and coke. It has been observed that distillation under moderate pressures of hydrogen eliminates the oxygen bridges, increases the liquid yield and also increases coke quality (9, 10, 11, 26, 27).

It is apparent that total hydrogenation of coal is uneconomic. However, a distillation process in which the hydrogen rich portions of the coal are retained as relatively low molecular weight hydrocarbons by hydrogenation in the presence of suitable catalysts might be worth considering.

Most investigators agree that the functional oxygen and sulfur groups control the yield of liquid products from coal. Van Krevelen states that the secondary reactions (polymerization to high molecular weight products) are especially noticeable with phenolic model materials. The cleaving of non-hydrocarbon bonds such as those of nitrogen, oxygen and sulfur, by hydrogen treating methods has recently become well established in the petroleum industry. For example, Blue and Spurlock have worked with cobalt molybdenum catalysts (30). Commercial catalytic hydrocracking methods include the Gulf HDS process (31), the Union Oil Unicracking process (32), the Standard Oil of California Isocracking process and the Universal Oil Lomax process, among others. The trend of increased hydrogen processing in industry has been discussed by Olson and Schneider (33) who mention hydrocracking of residual oils, hydrogenation of shale oil and gilsonite, hydrogenation of low gravity, high sulfur crudes and hydrogenation of aromatics to form superior jet fuels.

Some of these methods have been and are being applied to coal and to coal liquids (9, 27, 34) for the removal of the functional cross bonding groups for the production of maximum yields of liquids and of high quality coke. Van Krevelen for example, has worked on model material pyrolysis using the hydrogen donor materials suggested by Orchin and Storch to increase liquid yields and to minimize the polymerization-condensation reactions promoted by hydroxyl groups (4). The Varga process (35) and the Lozovoi process (36) are two additional examples of the use of hydrocracking techniques to produce high octane gasoline and other liquids from coal, primary tars, shale oil and high asphalt crude oil residues. Catalytic methods discussed by Flinn (37), Haensel (38) and Topchiev (39) are applicable to coal and coal liquids.

The high liquid yields made possible by hydrocracking-hydrotreating distillation of high volatile coals plus the marketability of the residual coke make it apparent that there will be a smooth and gradual transition from conventional petroleum refining to coal refining as the economic picture becomes favorable.

BIBLIOGRAPHY

(1) Smirnov, R. N., "Contemporary Representation of Coal Structure," Advances in Chemistry, B. 28, No. 7, 1959, (Inst. Fossil Fuels, Moscow, A. Review with 113 references through 1958), Translated by V. Fredricks.

(2) Lyon, Lloyd and Hill, George Richard, Ed., "The Structure and Chemistry of High Volatile Coals; The Catalytic Conversion of High Volatile Coals by Hydro-Catalytic Methods to Liquids and Coke". University of Utah Engineering Experiment Bulletin No. 109, Vol. 51, No. 26.

(3) Friedel, R. A., Queiser, J. A., "Ultra-Violet-Visible Spectrum and the Aromaticity of Coal," Fuel, London, Vol. 38, 1959, pp. 369-79.

(4) Van Krevelen, D. W., Waterman, H. I., Wolfs, P. M. J., Part I to VII - Brennstoff-Chemie, V. 40, 1959, Special Reference V - "Pyrolysis of Model Materials with Functional Groups," and VII - "Application to Mineral Coal of Understanding Attained," Translated by V. Fredricks.

(5) Roy, M. M., "Chromatographic Analysis of Coal Extracts Prepared from Assam Coal," Fuel, London, Vol. 36, pp. 344-54.

(6) Blom, L., Edelhausen, L., Van Krevelen, D. W., "Chemical Structure and Properties of Coal XVIII- Oxygen Groups in Coal and Related Products," Fuel, London, Vol. 36, 1957, pp. 135-58.

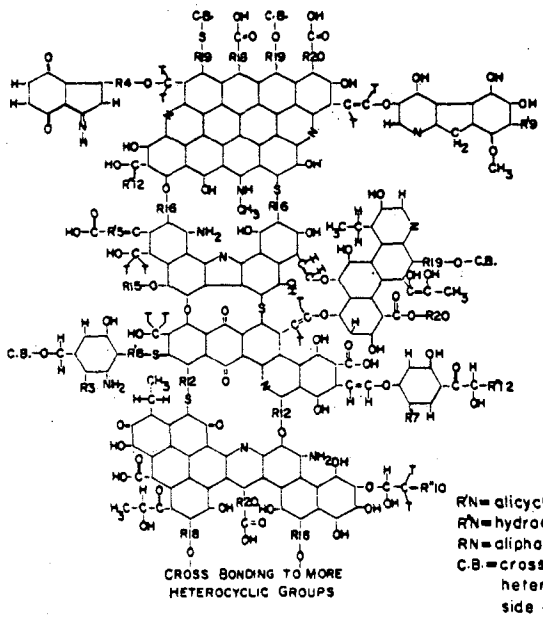
(7) Brooks, J. D., Maher, T. P., "Acidic Oxygen-Containing Groups in Coal," Fuel, London, Vol. 36, pp. 51-62.

(8) Golumbic, C., Anderson, J. B., Orchin, M., Storch, H. H., "Solvent Extraction of Coal by Aromatic Compounds at Atmospheric Pressure," U.S. Bureau of Mines, R. I. 4662, March 1950.

(9) Orchin, M., Storch, H. H., "Solvation and Hydrogenation of Coal," Ind. Eng. Chem. Vol. 40, No. 8, August 1948, pp. 1385-89.
(10) Orchin, M., Goldbach, G. L., Wolak, M., Storch, H. H., "Coal Hydrogenation. The Effect of Variations in the Coal-to-Vehicle Ratio," U. S. Bureau of Mines, R. I. 4499, July 1949.
(11) Orchin, M., Golumbic, C., Anderson, J. E., Storch, H. H., "Studies of the Extraction and Coking of Coals and Their Significance in Relation to its Structure," U. S. Bureau of Mines Bull., 505, 1951.
(12) LeMaire, G. W., "A Study of Asphalt and Asphaltic Materials," Quarterly of the Colo. Sch. of Mines, Vol. 48, No. 2, April 1953.
(13) State of Utah, "Low-Temperature Carbonization of Utah Coals," May 1939.
(14) Nelson, W. L., Petroleum Refining Engineering, Fourth Edition, McGraw-Hill Book Company, Inc., New York, 1958.
(15) Gomez, M., Goodman, J. B., Parry, V. F., "Low-Temperature Tar from Fluidized Carbonizing Reactors," U.S. Bureau of Mines, R. I. 5302, Feb. 1957.
(16) Gomez, M., Goodman, J. B., Parry, V. F., "General Properties of Low-Temperature Tar," U. S. Bureau of Mines Bull. 569.
(17) Lewis, H. R., "Paraffins in Low Temperature Tar From Fluidized Carbonization Process," Chemical and Industry, London, August 15, 1959, (National Coal Board, Stoke Orchard, England) pp. 1049-50.
(18) Given, P. H., "The Distribution of Hydrogen in Coals and Its Relation to Coal Structure," Fuel, London, Vol. 39, 1960, pp. 147-53.
(19) Brown, J. K., "Infra-red Spectra of Solvent Extracts of Coals," Fuel, London, Vol. 38, 1959, pp. 55-63.
(20) Brown, J. K., Ladner, W. R., Sheppard, N., "A Study of the Hydrogen Distribution in Coal-like Materials by High-Resolution Nuclear Magnetic Resonance Spectroscopy 1 - The Measurement and Interpretations of the Spectra," Fuel, London, Vol. 39, 1960, pp. 79-86. "II - A Comparison With Infra red Measurements and the Conversion to Carbon Structure," Fuel, London, Vol. 39, 1960, pp. 87-95.
(21) Van Krevelen, D. W., Ghermin, H. A. G., Schuyer, J., "XIX - Revaluation of the Structural Parameters of Vitrinites," Fuel, London, Vol. 36, pp. 313-20. (1957)
(22) Fitzgerald, D., Van Krevelen, D. W., "XXI - The Kinetics of Coal Carbonization," Fuel, London, Vol. 38, 1959, pp. 17-37.
(23) Wolfs, P. M. J., Van Krevelen, D. W., Waterman, H. I., "Chemical Structure and Properties of Coal XXV - The Carbonization of Coal Models," Fuel, London, Vol. 39, 1960, pp. 25-38.
(24) Dryden, I. G. C., "Chemical Structure of Coals: A Method for Comparing Data of Different Origins and for Testing Sets of Data for Self-Consistency," Fuel, London, Vol. 37, 1958, pp. 444-68.

(25) Hood, A., Clerc, R. J., O'Neal, M. J., "The Molecular Structure of Heavy Petroleum Compounds," Journal of the Institute of Petroleum, Vol. 45, No. 426, June 1959, pp. 168-73.
(26) Pevere, E. F., Arnold, G. B., U. S. Patent 2,595,979, June 5, 1952.
(27) Franke, N. W., Crowley, E. L., Elder, H. S., "Solvent Extraction of Lignite and Carbonization of Lignite Extracts," Ind. Eng. Chem., Vol. 49, No. 9, Sept. 1957, pp. 1402-8.
(28) Berkowitz, N., "Dispersibility of Coal in a Supersonic Field," Nature, Vol. 163, May 21, 1949, pp. 809-10.
(29) Berkowitz, N., "Mechanism of Coal Pyrolysis 1 - On the Nature and Kinetics of Devolatilization," Fuel, London, Vol. 39, 1960, pp. 47-58.
(30) Blue, E. M., Spurlock, B., "Cobalt-Moly Catalyst," Chem. Eng. Prog., Vol. 56, No. 4, April 1960, pp. 54-9.
(31) Beuther, H., Flinn, R. A., "Gulf HDS Turns Resid Into Cat Feed," Petroleum Refiner, Vol. 39, No. 4, April 1960, pp. 143-48.
(32) Hansford, R. C., Reeg, C. P., Wood, F. C., Vaell, R., "Unicracking," Oil and Gas Journal, Vol. 58, No. 16, April 18, 1960, pp. 104-6.
(33) Olson, H. N., Schneider, South West Engineering Co., "Big Future for Hydrogen Processing," Petroleum Refiner, Vol. 39, No. 4, April 1960.
(34) Lyon, Lloyd B., Patents Pending.
(35) Varga, J., Karolyi, J., Steingósznev, P., Zalai, A., Birthler, R., Rabo, Gy., Nagynyomasu Kieserleti Intezet, Budapest. "Hydrocracking Tried on Larger Scale," Petroleum Refiner, Vol. 39, No. 4, pp. 182-3.
(36) Lozovoi, A. V., Muselevich, D. L., Blonskaye, A. I., Ravikovich, T. M., Titova, T. A., "High Octane Gasoline From Coal and Primary Tars," USSR 111, 769, June 25, 1958.
(37) Flinn, R. A., Larson, O. A., Beuther, H., "The Mechanism of Catalytic Hydrocracking," Ind. & Eng. Chem., Vol. 53, No. 2, Feb. 1960, pp. 153-56.
(38) Haensel, V., Berger, C. U., Advance Petroleum Chemistry and Refining, Interscience Publishers, Inc., Edited by K. A. Kobe and J. J. McKetta, Vol. 1, 1958.
(39) Topchiev, A. V., "Boron Fluoride and Its Compounds as Catalysts in Organic Ehcmistry," International Series of Monographs on Organic Chemistry, Translated by J. T. Greaves , Pergamon Press, 1959.

TYPICAL CROSS BONDED STRUCTURE OF HIGH VOLATILE COALS



(High Volatile Coal Analyses)

H= 4 to 8% by wt.
C= 70 to 93% by wt.
N= ·5 to 2% " "
S= ·5 to 3% " "
O= 7 to 24% " "

R'N= alicyclics of N carbons.
R̂N= hydroaromatics of N carbons.
RN= aliphatic side chain of N carbons.
C.B.= cross bonding by O or S to new heterocyclic groups with long side chains.
T= tetrahedral 3 dimensional C-C bonds, C-O bonds and C-S bonds.

PROPOSED MODEL

Fig. 1